Temperature Dependence of Exciton Dynamics in Poly(di-n-hexylsilane)

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We have investigated the temperature dependence of the time response of luminescence intensity in poly(di-*n*-hexylsilane) films in the range between 4 and 300 K and in solution at 4 and 295 K. In both samples, rise and decay times strongly depend on observed energy at 4 K. The rise time is about 100 ps at the peak energy. At about 110 K in films and at 295 K in solution, rise times become small and decay times become less dependent on energy with increasing temperature. In films at 295 K, decay times are independent of energy and rise times becomes less than 5 ps. These results are explained by the exciton dynamics governed by the competing processes of phonon scattering and radiative decay in disordered linear chains. It is found that the time response is more sensitive to temperature in films than in solution by the factor of 3. This difference is ascribed to the presence and the absence of interchain exciton transfer in films and in solution, respectively.

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Understanding exciton dynamics in luminescent conjugated polymers is important both for the quasi-one-dimensional physics[1] and for developing light-emitting devices.[2,3] Among various conjugated polymers, a σ-conjugated polymer of poly(di-*n*-hexylsilane) (PDHS) has remarkable features of the high luminescence efficiency of near unity[4,5] and the extremely small exciton-phonon coupling.[6] Therefore, PDHS is a suitable test bench for investigating the one-dimensional dyanmics of excitons in linear chains via optical spectroscopies.[7–18] Excitons are nearly free from lattice relaxation, but are localized by conformal disorder of polymer chains, as Anderson predicted,[19] which is a key factor for understanding the exciton dynamics in PDHS.

Early experiments of luminescence depolarization[9,10] had been interpreted by *the segment model*[9] phenomenologically, in which excitons migrate from shorter to longer segments. Recently, a microscopic description of exciton dynamics[7,8] has been proposed, based on *the one-dimensional Frenkel exciton model with disorder* (1DFEMD).[6] In this model, exciton states are localized by small continuous disorder without postulating the conformal defects. Exciton dynamics is governed by the competing processes of radiative decay to the ground state and phonon scattering between localized states. We proposed that *the matrix element for phonon scattering is given by the spatial overlap between the initial and final states of scattering*.[7] This treatment is successful to reproduce the time response of luminescence in PDHS films and in solution at 2 K, consistent with the absorption spectrum.[7] To test the theory in more detail, a systematic investigation of temperature dependence is necessary because the phonon scattering rate is affected by temperature.

In this paper we report the temperature dependence of absorption spectra, luminescence spectra, and the time response of luminescence intensity in PDHS films in the temperature range between 4 and 300 K and in solution at 295 K. It is found that, as temperature increases, rise times of luminescence intensity become small and that decay times become less dependent on observed energy, in both samples. In detail, however, the time response is more sensitive to temperature in films than in solution by the factor of 3. This temperature dependence agrees with the 1DFEMD (Refs. 7 and 11) qualitatively. Quantitative deviation is discussed on the basis of interchain exciton transfer in films.

The used PDHS had an average molecular weight (M_w) of 236 000 and a dispersion (M_w/M_n) of 1.30 with a monomodal distribution. M_w corresponds to the polymerization of 1180 di-n-hexylsilane units. Measurements were carried out for spin-coated films on quartz plates and for dilute solution in tetrahydrofran with a concentration of 50 mg/l, in which interaction between polymer strands is neglegible. Films were put on the cold finger of a He-flow-type cryostat (Oxford CF-1204) in which temperature was controlled in the range between 4 and 300 K. The solution was measured at 295 K in a quartz cell of 3 mm path length.

For absorption measurements, we used a deuterium lamp, a single monochromator, and a silicon diodes array as a detector. The spectral resolution was 5 meV. For luminescence measurements, the frequency-doubled output of pyridine-2 or rhodamine-6G dye lasers (Coherent 701-3) which are synchronously pumped by the doubled output of a mode-locked Nd:YAG (where YAG is yttrium aluminum garnet) laser is used. The pulse duration, the repetition, and the intensity of the excitation pulse were 6 ps, 76 MHz, and 1 pJ, respectively. Excitation density was kept below 1×10^9 photons cm^{-2} $pulse^{-1}$ to prevent nonlinear effects[22] and the photodegradation of samples. Luminescence from samples was spectrally resolved by a subtractive double monochromator (Jasco CT-25CD) and then detected by a photomultiplier or a synchroscan streak camera (Hamamatsu C1587). The spectral resolution was 5 and 10 meV for films and for solution, respectively. The instrumental response of the system with the streak camera was 30 ps. Since the time response depends on the quality of films within 25%, a series of measurements were carefully performed for the same film.

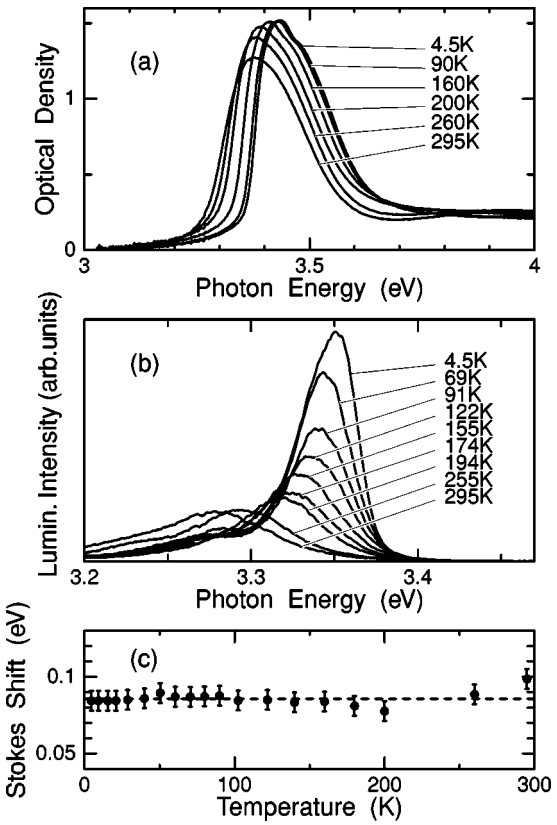

FIG. 1. Temperature dependence of absorption spectra (a), luminescence spectra (b), and Stokes shift (c) in PDHS films. In (c), the dotted line shows the fitting by a constant energy.

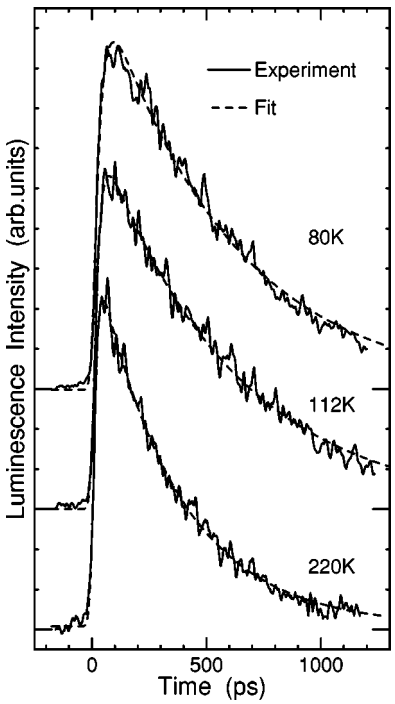

FIG. 2. Time responses of luminescence intensity in PDHS films at 80 K (upper), 112 K (middle), and 220 K (lower). Each time response is observed at the luminescence peak energy. Dotted lines show fitting curves with a rise time and a decay time.

Figure 1(a) shows the temperature dependence of absorption spectra of PDHS films in the range between 4.5 and 295 K. The peak energy of the lowest exciton band is 3.43 eV at 4.5 K. With increasing temperature, the peak slightly shifts to lower energy. The FWHM of the band is 0.19 eV at 4.5 K and becomes larger with increasing temperature approximately in the rate of 0.07 meV/K in the measured temperature range. In (b), the temperature dependence of luminescence spectra is shown. The luminescence peak also shifts to lower energy with increasing temperature. Stokes shifts, i.e., the difference between absorption and luminescence peak energies, are shown in (c). Up to 300 K, Stokes shifts are 85 ± 5 meV and are independent of temperature.

According to the 1DFEMD,[7,11] however, the peak energies of both absorption and luminescence are independent of temperature, in contrast to the above results. In real films, the temperature dependence of the absorption peak energy is ascribed to the following two changes. One is the change of the band-gap energy caused by the change in bond length and the other is the change of the degree of conformal disorder of polymer chains. In the 1DFEMD,[6,11] the enhancement of disorder causes not only the redshift of the peak energy but also the broadening of the bandwidth. Since the change in the bandwidth is only 2%, the contribution of disorder for the peak shift is small. Thus, the shift of absorption peak energy is mainly ascribed to the change in the band-gap energy. We note that the temperature range that we discuss here is far from the phase transition temperature of 350 K.[20] The temperature dependence of the luminescence peak energy is also attributed to the change of band-gap energy because the Stokes shift is independent of temperature. Therefore, it is considered that the temperature change simply shifts the energy of exciton states and does not significantly affect the nature of exciton states. The intersite exciton transfer energy and the degree of conformal disorder are approximately independent of temperature.

Figure 2 shows the time responses of luminescence intensity in films observed at the peak energies at 80 K (upper), 112 K (middle), and 220 K (lower). Using the deconvolution technique with the instrumental response, each time response is well fitted by an exponential rise time and an exponential decay time, as shown by dotted lines. Rise times and decay times are estimated to be 100 and 500 ps, respectively, at 80 K and 20 and 600 ps at 112 K. At 220 K, the rise time is less than 5 ps which is the limit of resolution by the deconvolution technique. The decay time is 350 ps.

We have measured time responses at various observed energies. Rise and decay times are functions of both energy and temperature. Below 80 K, rise and decay times are almost independent of temperature although the peak energy shifts slightly. Figure 3(a) displays rises and decay times at 80 K as functions of observed energy, respectively, by open and closed circles. The luminescence spectrum is also shown by the solid line for comparison. The arrow indicates the excitation energy at 3.44 eV. Rise and decay times are larger at the lower energy, although both times saturate at the energy lower than the peak energy at which they take maximum values of 100 and 450 ps, respectively. This energy dependence of rise and decay times is well understood by the

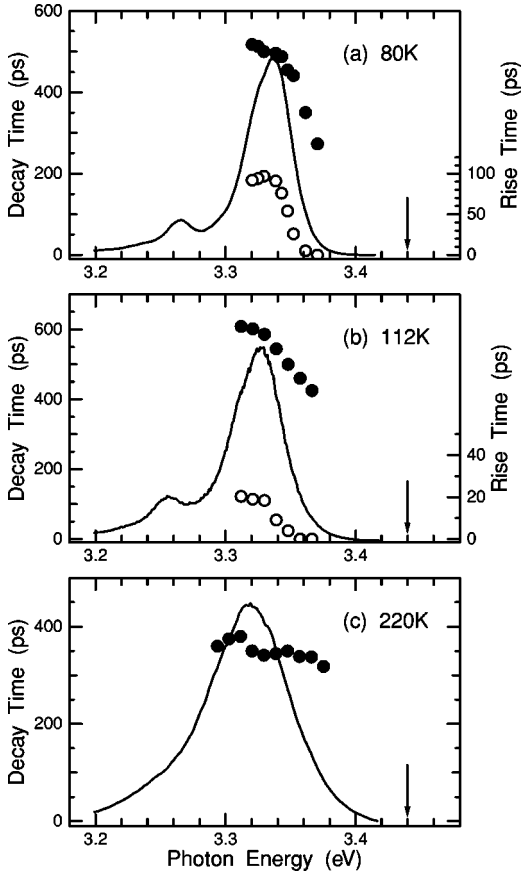

FIG. 3. Rise and decay times of luminescence intensity in PDHS films as functions of observed energy at 80 K (a), 112 K (b), and 220 K (c). Rise and decay times are shown by open and closed circles, respectively, and to be referred to right and left ordinates, respectively. Luminescence spectra are shown by solid lines in arbitrary units for comparison. Arrows indicate the excitation energy.

competing processes of radiative decay and phonon scattering of excitons between states localized by the conformal disorder of polymer chains. Rise times correspond to the transition times from initially photoexcited states to luminescent states by a few to several times of phonon scattering.[7] Decay times are determined by the radiative decay rate and the energy relaxation rate determined by the phonon scattering rate. The 1DFEMD predicts that the radiative decay rate is the largest at the peak energy and is smaller in the higher and the lower energies than the peak energy.[11] This energy dependence is rather in contrast to the observed distribution of decay times. Thus, it is considered that the smaller decay times at the higher energy is due to the larger phonon scattering rate at the higher energy. The exciton at the higher energy has the more available final states for phonon scattering at low temperature. In our previous paper,[7] the time response at 2 K are well reproduced by our formula based on the 1DFEMD.

With increasing temperature above 80 K, rise times become small gradually and decay times becomes less dependent on observed energy. At 112 K, the rise time at the peak energy is 20 ps and the energy dependence of decay times is weak compared with that at 80 K, as shown in Fig. 3(b). At the higher temperature of 220 K shown in Fig. 3(c), rise times are less than 5 ps (not shown) and decay times are about 350 ps, independent of observed energy. The smaller rise times at the higher temperature are explained by the increase of the phonon scattering rate. The energy independence of decay times is explained by *the thermal distribution* of excitons, in which the net rate of exciton relaxation is independent of energy. This implies that *the effective local level spacing*, i.e., the energy difference between the lowest and the second lowest exciton states at an arbitrary position in polymer chains, is about 220 K (19 meV) in PDHS films. Since the conformal disorder of polymer chains makes exciton states be localized and be discrete,[11] the energy which excesses the local level spacing is required for the thermal distribution.

Thermal distribution of excitons in PDHS films are previously indicated by the photoconductivity experiment by Kepler and Soos[12] at room temperature. They concluded that excitons are well mobile within their lifetimes. The diffusion constant for excitons was estimated to be more than 0.05 cm^{-2} s^{-1}. This high mobility is explained by the thermal distribution of excitons which prevent excitons to be trapped in some disorder-induced local potential minima.

This temperature dependence of the time response in films qualitatively agrees with our theory[7,11] based on the 1DFEMD. The theory predicts that the decrease of rise times occurs at around 300 K and the thermal distribution of excitons is realized at about 600 K.[11] This prediction is qualitatively consistent with the experimental results, but is *insensitive* to temperature in comparison with the experimental results by the factor of 3. This deviation is ascribed to the *absence* of the *interchain exciton transfer* in the 1DFEMD. In films, the interchain exciton transfer is likely because the possible smallest distance between two chains is estimated to be 0.7 nm.[21] To examine the interchain exciton transfer in films, comparison with the results for isolated strands in dilute solution is important.

In glassy dilute solution at low temperature, the time response of luminescence intensity is quantitatively close to that in films. At 2 K,[7] absorption and luminescence peak energies are 3.52 and 3.45 eV, respectively. It has been clarified that rise and decay times are larger at the lower energy and take 100 and 300 ps, respectively, at the peak energy.

Figure 4 shows the absorption and luminescence spectra of PDHS solution at 295 K by dashed and solid lines, respectively. The arrow indicates the excitation energy. The peak energy of absorption is 3.9 eV, which is about 0.4 eV higher than that at 2 K. This difference is mainly caused by the thermochromic transition at about 250 K.[23] Time responses of luminescence intensity are also measured as functions of observed energy and are analyzed by an exponential rise time and an exponential decay time with the convolution technique. In Fig. 4, rise and decay times are shown by open and closed circles, respectively. Rise and decay times take the smaller values at the higher energy, and are 20 and 150 ps, respectively, at the peak energy. This decay time is about a half of that at 2 K. This is due to the increase of the nonradiative decay rate.[5] The rise time is one-fifth as large as

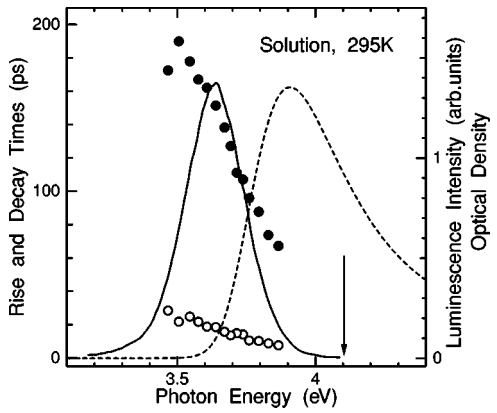

FIG. 4. Absorption spectrum (the dashed line), the luminescence spectrum (the solid line), and the time response of luminescence intensity in PDHS solution at 295 K. Rise and decay times as functions of observed energy are shown by open and closed circles, respectively. The arrow indicates the excitation energy.

that at 2 K (Ref. 7) and approximately the same as at 112 K in films. It is interesting that the time response in solution are less sensitive to temperature than that in films, although the time responses at 2 and 295 K in solution are difficult to be rigorously compared because of the thermochromic transition at the intermediate temperature between them.

Unfortunately, the precise prediction of the temperature dependence in solution is impossible because the theory does not take the thermochromic transition[21] into account. However, we tentatively suppose that the transition does not affect the nature of the exciton dynamics in solution substantially. The experimental result in solution rather agrees with the prediction[11] of rise and decay times by the 1DFEMD (Ref. 7) which does not take the interchain coupling into account. Therefore, it is considered that the disagreement in the temperature sensitivity between the films and the 1DFEMD is ascribed to the presence of the interchain exciton transfer in the real films because interchain exciton transfer is absent in solution. Interchain exciton transfer causes the extension of exciton wave functions to neighboring PDHS chains.[7,22] This enables excitons to jump to neighboring chains and thus excitons have more available states for phonon scattering in films. The effective local density of states is larger, i.e., the *local level spacing* is smaller, in films. To realize the thermal distribution, it is required that the thermal energy excesses the local level spacing. The effective local level spacing is approximately estimated to be 19 meV for films and more than 30 meV (295 K) for solution.

In summary, in order to investigate the temperature dependence of the exciton dynamics in PDHS, we have performed the measurements of absorption spectra, luminescence spectra, and the time response of luminescence intensity in the range between 4 to 300 K for films and at 295 K for solution. In films, rise times of luminescence intensity depend on observed energy and are 100 ps at the peak energy at the temperature below 80 K. At higher temperature, rise times become small. Above 200 K, rise times are less than 5 ps and decay times are independent of observed energy. In solution, the rise time at the peak energy is 20 ps even at 295 K. In both samples, the decrease of rise times at the higher temperature is caused by the increase of the phonon scattering rate. The energy-independent decay time in films is explained by the thermal distribution of excitons. These results in both samples agree with the theory based on the 1DFEMD, although the time response in films is more sensitive to temperature than what theory predicts by the factor of 3. This deviation is explained by the interchain exciton transfer in films.

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